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Synthesis, structure and reactivity of cationic base-stabilized gallyleneiron complexes[†]

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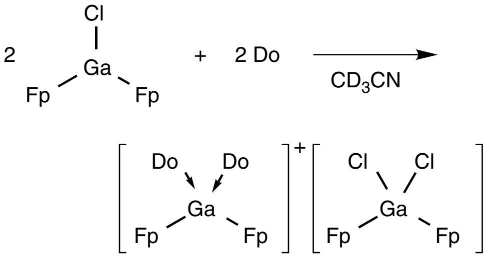
Addition of 2,2′-bipyridine (bpy) to an acetonitrile solution of dichlorogallyliron complex $\mathrm{FpGaCl_2}$ (1: Fp = $(\eta\text{-}C_5H_5)Fe(CO)_2$) afforded almost quantitatively a salt consisting of a cationic base-stabilized gallylene complex $[\mathrm{FpGaCl{\cdot}bpy}]^+$ ($[\mathbf{3a}]^+$) and an anionic complex $[\mathrm{FpGaCl_3}]^-$ ($[\mathbf{4}]^-$). Reaction of $\mathrm{Fp'GaCl_2}$ (Fp′ = Fp (1), Fp* (2); Fp* = $(\eta\text{-}C_5Me_5)Fe(CO)_2$) with $\mathrm{NaBPh_4}$ in the presence of a bidentate donor ($\mathrm{Do_2}$) gave $[\mathrm{Fp'GaCl{\cdot}Do_2}]\mathrm{BPh_4}$ where $\mathrm{Do_2}$ was bpy or 1,10-phenanthroline (phen). These cationic complexes may be useful precursors for the synthesis of gallyleneiron complexes with various substituents on the gallium atom. Indeed, reaction of $[\mathrm{Fp^*GaCl{\cdot}phen}]\mathrm{BPh_4}$ ($[\mathbf{5b}]\mathrm{BPh_4}$) with $\mathrm{NaS}^p\mathrm{Tol}$ or $\mathrm{Me_3SiS}^p\mathrm{Tol}$ afforded the gallyleneiron complex $[\mathrm{Fp^*GaS}^p\mathrm{Tol{\cdot}phen}]\mathrm{BPh_4}$ ($[\mathbf{6}]\mathrm{BPh_4}$), the first example of a gallium–transition metal complex having a thiolate group on the gallium atom. The molecular structures of $[\mathbf{5b}]\mathrm{BPh_4}$ and $[\mathbf{6}]\mathrm{BPh_4}$ were determined by single crystal X-ray diffraction. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: gallylene iron complexes; gallyl iron complexes; dehalosilylation reaction

INTRODUCTION

Transition metal complexes containing metal–gallium bonds have attracted ongoing interest in organometallic chemistry.[1] Synthesis of terminal gallylene (gallanediyl) complexes L_nMGaR that contain a bi-coordinate gallium atom has been one of the current topics.[2,3] A number of base-stabilized terminal gallylene complexes $L_nMGaR{\cdot}Do_2$ (Do = Lewis base) have also been synthesized.[4–12]

We recently reported that addition of a Lewis base ($\mathrm{Do_2}$ = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, (4-(dimethylamino)pyridine)$_2$) to an acetonitrile solution of a diiron complex $\mathrm{Fp_2GaCl}$ (Fp = $(\eta\text{-}C_5H_5)Fe(CO)_2$) caused a base-induced ligand reorganization reaction to produce a salt consisting of a diiron cation bridged by a $\mathrm{Ga{\cdot}Do_2}$ fragment and a μ-$\mathrm{GaCl_2}$ diiron anion (Eqn (1)):[13]



(1)

The reaction of $\mathrm{Fp_2GaCl}$ with a Lewis base in the presence of $\mathrm{NaBPh_4}$ in acetonitrile gave $[\mathrm{Fp_2}(\mu\text{-}\mathrm{Ga{\cdot}Do_2})]^+\ \mathrm{BPh_4}^-$. It would be important to know if addition of a Lewis base to a mononuclear complex $\mathrm{FpGaCl_2}$ causes a base-induced ligand reorganization reaction similar to that given in Eqn (1).

Here, we report that the reactions of $\mathrm{FpGaCl_2}$ with bpy or phen did in fact induce a ligand reorganization reaction to afford $[\mathrm{FpGaCl{\cdot}Do_2}]^+\ [\mathrm{FpGaCl_3}]^-$ containing the first reported cationic gallylene complex ion. Furthermore, the reaction of $\mathrm{Fp'GaCl_2}$ (Fp′ = Fp (**1**), Fp* (**2**); Fp* = $(\eta\text{-}C_5Me_5)Fe(CO)_2$) with bpy or phen in the presence

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[†] Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.

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of $\mathrm{NaBPh_4}$ was found to produce $\mathrm{[Fp'GaCl{\cdot}Do_2]^+BPh_4^-}$. These cationic complexes may be useful precursors for the synthesis of gallyleneiron complexes with various substituents on the gallium atom. To demonstrate this, reaction of $\mathrm{[Fp^*GaCl{\cdot}phen]BPh_4}$ with $\mathrm{NaS}^p\mathrm{Tol}$ or $\mathrm{Me_3SiS}^p\mathrm{Tol}$ was carried out, which afforded thiolate-substituted product $[\mathrm{Fp^*GaS}^p\mathrm{Tol{\cdot}phen}]^+$ $\mathrm{BPh_4^-}$. An improved synthesis of $\mathrm{Fp'GaCl_2}$ is also described in this paper.

RESULTS AND DISCUSSION

Dichlorogallyliron complex $\mathrm{FpGaCl_2}$ (**1**) has been synthesized by a salt elimination reaction between $\mathrm{GaCl_3}$ and KFp.[14] However, repetition of the procedure revealed that the product **1** was always accompanied by $\mathrm{Fp_2}$ as an impurity. The separation of these two products was rather difficult, and the isolated yield of pure **1** was low. We found that a dehalosilylation reaction between $\mathrm{FpSiMe_3}$ and $\mathrm{GaCl_3}$ at room temperature in hexane or toluene afforded instantly analytically pure yellow crystals of **1** (Eqn (2)) in almost quantitative yield. $\mathrm{Fp^*GaCl_2}$ (**2**) was also synthesized almost quantitatively by the reaction of $\mathrm{GaCl_3}$ and $\mathrm{Fp^*SiMe_3}$ in hexane at room temperature.

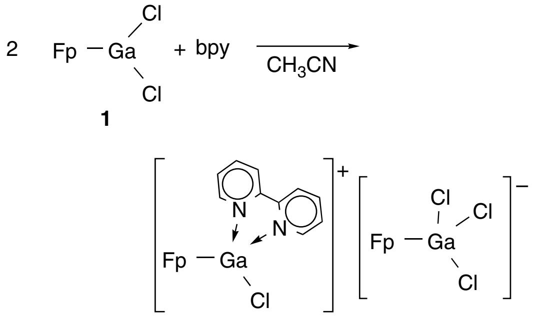
$$\mathrm{GaCl_3} + \mathrm{Fp'SiMe_3} \xrightarrow[\text{hexane}]{\text{r. t.}} \underset{-\,\mathrm{Me_3SiCl}}{} \ \mathrm{Fp'GaCl_2} \qquad (2)$$

Fp' = Fp (**1**), Fp* (**2**)

The molar ratio of $\mathrm{GaCl_3}$ and $\mathrm{Fp'SiMe_3}$ is unimportant for the reaction given in Eqn (2), but the reaction temperature is critical. Reaction of $\mathrm{GaCl_3}$ with an excess amount of $\mathrm{Fp'SiMe_3}$ at room temperature produced no unwanted products ($\mathrm{Fp'_2GaCl}$[14,15] or $\mathrm{Fp'_3Ga}$[15]) at all, but gave almost quantitatively **1** (Fp′ = Fp) and **2** (Fp′ = Fp*). However, heating the solution containing $\mathrm{GaCl_3}$ and an excess amount of $\mathrm{FpSiMe_3}$ at 100 °C for 3 days produced almost quantitatively $\mathrm{Fp_2GaCl}$ (Eqn (3)). In contrast to the formation of $\mathrm{Fp_2GaCl}$, conversion of **2** to $\mathrm{Fp^*_2GaCl}$ proceeded much more slowly. Only a trace amount of $\mathrm{Fp^*_2GaCl}$ was detected even after heating a toluene solution of **2** and excess $\mathrm{Fp^*SiMe_3}$ at 100 °C for 1 week.

$$\underset{\mathbf{1}}{\mathrm{FpGaCl_2}} + \mathrm{FpSiMe_3} \xrightarrow[\text{toluene}]{100\ ^\circ\mathrm{C}} \underset{-\,\mathrm{Me_3SiCl}}{} \ \mathrm{Fp_2GaCl} \qquad (3)$$

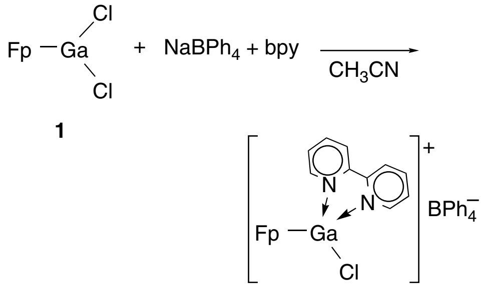
Addition of bpy to an acetonitrile solution of **1** afforded a salt consisting of a cationic gallyleneiron complex $\mathrm{[FpGaCl{\cdot}bpy]^+}$ ($[\mathbf{3a}]^+$) and an anionic complex $\mathrm{[FpGaCl_3]^-}$ ($[\mathbf{4}]^-$) (Eqn (4)).



(4)

[3a][4]

The product was isolated as orange crystals **[3a][4]** in 92% yield and was fully characterized by NMR, IR and mass spectroscopy, and elemental analysis. This reaction is a ligand reorganization reaction induced by coordination of a bpy molecule. Complex $[\mathbf{3a}]\mathrm{BPh_4}$ was synthesized by the reaction of **1** with $\mathrm{NaBPh_4}$ in the presence of bpy (Eqn (5)). The complexes $\mathrm{[Fp'GaCl{\cdot}Do_2]BPh_4}$ (**3b**: Fp′ = Fp, $\mathrm{Do_2}$ = phen; **5a** Fp′ = Fp*, $\mathrm{Do_2}$ = bpy; **5b**: Fp′ = Fp*, $\mathrm{Do_2}$ = phen) were also synthesized in moderate yields by the reaction of $\mathrm{Fp'GaCl_2}$ with $\mathrm{NaBPh_4}$ in the presence of the corresponding bidentate donor.



(5)

$[\mathbf{3a}]\mathrm{BPh_4}$

X-ray crystal structure analysis of $[\mathbf{5b}]\mathrm{BPh_4{\cdot}2CH_3CN}$ revealed that the gallium center adopts a distorted tetrahedral geometry where the Fe–Ga–Cl angle is 122.54(3)° (Fig. 1). The Fe–Ga bond length (2.3047(4) Å) is considerably shorter than those of the cationic diiron complex $[\mathrm{Fp_2}(\mu\text{-}\mathrm{Ga{\cdot}bpy})]^+$ (2.3969(16) and 2.4037(14) Å),[13] but within the range of bond lengths reported previously for neutral base-stabilized terminal gallyleneiron complexes (2.27–2.34 Å).[4,5] If silyl ligands in silyl complexes bear electron-withdrawing substituents, short M–Si bond lengths have been observed. The findings have been explained as the enhancement of π-back donation from the metal center to the silyl silicon atom.[16,17] The short Fe–Ga bond length found in $[\mathbf{5b}]^+$, compared with those in $[\mathrm{Fp_2}(\mu\text{-}\mathrm{Ga{\cdot}bpy})]^+$, is also likely attributable to the electron-withdrawing nature of the chlorine atom in $[\mathbf{5b}]^+$. The Ga–N bond lengths (2.057(2) and 2.065(2) Å) in $[\mathbf{5b}]^+$ are also shorter than those of $[\mathrm{Fp_2}(\mu\text{-}\mathrm{Ga{\cdot}bpy})]^+$ (2.074(5) and 2.091(5) Å)[13] and within the range of those

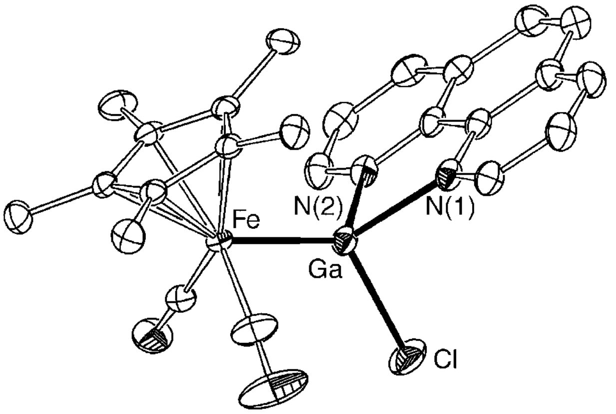
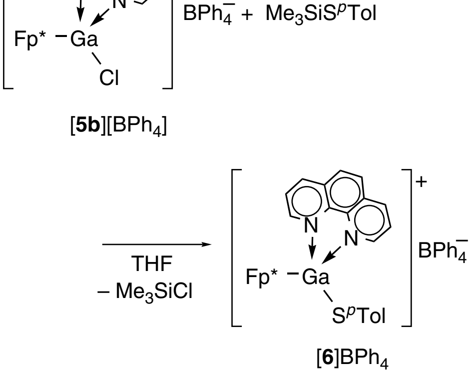


Figure 1. ORTEP drawing of the cation portion of [**5b**]BPh$_4$·2CH$_3$CN. Thermal ellipsoids are depicted at the 50% probability level. Selected bond lengths: Fe–Ga = 2.3047(4), Ga–N(1) = 2.057(2), Ga–N(2) = 2.065(2), Ga–Cl = 2.2090(7) Å. Selected bond angles: Fe–Ga–Cl = 122.54(3)°, N(1)–Ga–N(2) = 80.96(8)°.

reported for amine-coordinated metal–gallium complexes (1.97–2.40 Å).[18–22] The Ga–Cl bond length (2.2090(7) Å) is comparable to those observed for metal–chlorogallium complexes (2.18–2.29 Å).[23,24]

The cationic terminal gallyleneiron complexes [**3**]$^+$ and [**5**]$^+$ bear a chlorine atom on the gallium atom and may be useful precursors for the synthesis of gallylene complexes with various substituents on its gallium atom. Indeed, reaction of [**5b**]BPh$_4$ with NaS^{p}Tol in tetrahydrofuran (THF) afforded [Fp*GaS^{p}Tol·phen]BPh$_4$ ([**6**]BPh$_4$) in 39% yield. Complex [**6**]BPh$_4$ can also be synthesized quantitatively by a dehalosilylation reaction of [**5b**]BPh$_4$ with a small excess of Me$_3$SiS^{p}Tol in THF at room temperature (Eqn (6)). In the latter case, analytical pure crystals were isolated in excellent yield (99%) by evaporation of volatiles from the reaction mixture. Complex [**6**]BPh$_4$ is the first example of a gallium–transition metal complex having a thiolate group on the gallium atom (cubane-type cluster [FpGaS]$_4$ with Ga$_4$S$_4$ core is the unique example of a gallium–transition metal complex containing a Ga–S bonding).[25]



(6)

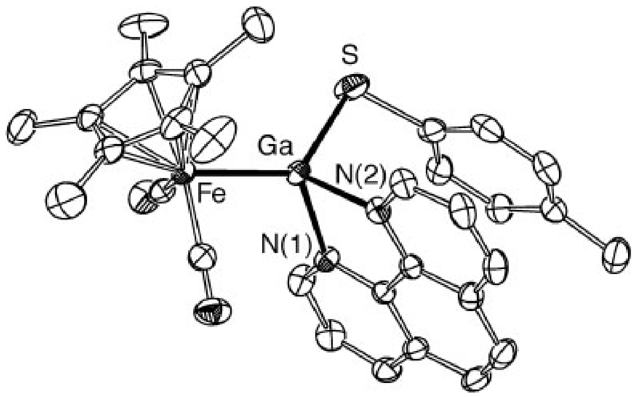


Figure 2. ORTEP drawing of the cation portion of [**6**]BPh$_4$. Thermal ellipsoids are depicted at the 50% probability level. Selected bond lengths: Fe–Ga = 2.3256(5), Ga–N(1) = 2.068(2), Ga–N(2) = 2.069(2), Ga–S = 2.2722(8) Å. Selected bond angles: Fe–Ga–S = 126.42(3)°, N(1)–Ga–N(2) = 79.97(9)°.

Crystal structure analysis of [**6**]BPh$_4$ (Fig. 2) revealed that the Fe–Ga bond length (2.3256(5) Å) is slightly longer than that of [**5b**]$^+$ (2.3047(4) Å), which is attributable to the weaker electron-withdrawing nature of the thiolate group compared with the chlorine atom. The Ga–S bond length (2.2722(8) Å) is comparable to those of previously reported thiolatogallium compounds (2.20–2.27 Å).[26–28] The Ga–N bond lengths (2.068(2) and 2.069(2) Å) are almost identical to those of [**5b**]$^+$ (2.057(2) and 2.065(2) Å). The inter-plane distance between the *p*-tolyl group and the phen ligand is *ca* 3.51 Å, which indicates the existence of a π-stacking interaction between the aromatic ring systems. A similar phenomenon to this has been reported for a base-stabilized silylyne complex [(η-C$_5$Me$_5$)Ru(PMe$_3$)$_2$SiS^{p}Tol·phen](OTf)$_2$,[29] which is isoelectronic to [**6**]$^+$.

CONCLUSIONS

The results of this study show that mononuclear FpGaCl$_2$ does indeed undergo a ligand reorganization reaction with bpy or phen to afford [FpGaCl·Do$_2$]$^+$[FpGaCl$_3$]$^-$, containing the first reported cationic gallylene complex ion. Furthermore, reaction of Fp′GaCl$_2$ with bpy or phen in the presence of NaBPh$_4$ was found to produce the complexes [Fp′GaCl·Do$_2$]$^+$BPh$_4$$^-$, which appear to be useful precursors for the synthesis of gallyleneiron complexes with various substituents on the gallium atom. To demonstrate this, thiolate-substituted product [Fp*GaS^{p}Tol·phen]$^+$BPh$_4$$^-$ was synthesized. An improved synthesis of Fp′GaCl$_2$ was also demonstrated.

EXPERIMENTAL

General

All manipulations were performed using standard Schlenk tube techniques under nitrogen or argon atmosphere, vacuum line techniques, or a drybox under a nitrogen atmosphere. Hexane, toluene, and THF were dried by refluxing over sodium benzophenone ketyl followed by distillation under a nitrogen atmosphere. Acetonitrile and acetonitrile-d_3 were dried over CaH_2 and distilled prior to use. Bpy and phen were purified by recrystallization from a hexane or toluene solution. $FpSiMe_3$[30] and Fp^*SiMe_3[31] were prepared according to the literature procedures. NMR spectra were recorded on a Bruker ARX-300 Fourier transform spectrometer at room temperature. IR spectra were obtained on a HORIBA FT-200 or FT-730 spectrometer at room temperature. Mass spectra were recorded on a JEOL HX-110 spectrometer at the Instrumental Analysis Center for Chemistry, Tohoku University. Elemental analyses were also performed at the Instrumental Analysis Center for Chemistry, Tohoku University.

Synthesis

*Synthesis of $FpGaCl_2$ (**1**)*

To a hexane (5 ml) solution of $GaCl_3$ (0.36 g, 2.0 mmol) was added a hexane (10 ml) solution of $FpSiMe_3$ (0.50 g, 2.0 mmol) at room temperature with vigorous stirring for 3 min. Yellow crystals of **1** were formed instantly during the addition. The crystals were isolated by decantation, washed with hexane (5 ml), and dried under reduced pressure. Yield: 0.62 g (1.95 mmol, 98%). ^{1}H NMR (300 MHz, C_6D_6): δ, 4.09 (s, 5H, C_5H_5). ^{13}C NMR (75.5 MHz, C_6D_6): δ, 82.8 (C_5H_5). IR (C_6D_6): ν_{CO} 1952, 2002 cm^{-1}. MS (EI, 70 eV): m/z 318 (M^+, 12), 290 ($M^+ - CO$, 26), 262 ($M^+ - 2CO$, 68), 156 (CpFeCl, 100). Anal. Found: C, 26.69; H, 1.57. Calc. for $C_7H_5Cl_2FeGaO_2$: C, 26.47; H, 1.59%.

*Synthesis of Fp^*GaCl_2 (**2**)*

Complex **2** was obtained as pale yellow crystals by a procedure similar to the synthesis of **1** using Fp^*SiMe_3 (1.0 g, 3.1 mmol) and $GaCl_3$ (0.55 g, 3.1 mmol). Yield: 1.16 g (3.0 mmol, 96%). ^{1}H NMR (300 MHz, C_6D_6): δ, 1.49 (s, 15H, C_5Me_5). ^{13}C NMR (75.5 MHz, C_6D_6): δ, 9.8 ($C_5\mathit{Me}_5$), 95.2 (C_5Me_5), 214.2 (CO). IR (C_6D_6): ν_{CO} 1930, 1981 cm^{-1}. MS (EI, 70 eV): m/z 388 (M^+, 8), 351 ($M^+ - Cl$, 10), 332 ($M^+ - 2CO$, 13), 226 (Cp^*FeCl, 100). Anal. Found: C, 37.17; H, 4.05. Calc. for $C_{12}H_{15}Cl_2FeGaO_2$: C, 37.17; H, 3.90%.

*Synthesis of [FpGaCl·bpy][$FpGaCl_3$] ([**3a**][**4**])*

To an acetonitrile (3 ml) solution of $FpGaCl_2$ (0.20 g, 0.63 mmol) was added an acetonitrile (2 ml) solution of bpy (0.050 g, 0.32 mmol) at room temperature with vigorous stirring. The reaction mixture was stirred for 1 h. Volatiles were removed from the reaction mixture under reduced pressure. The residual solid was washed with toluene (5 ml) and dried under reduced pressure to give orange crystals of [**3a**][**4**]. Yield: 0.23 g (0.29 mmol, 92%). ^{1}H NMR (300 MHz, acetonitrile-d_3): δ, 4.82 (s, 5H, C_5H_5), 5.11 (s, 5H, C_5H_5), 8.08 (m, 2H, bpy), 8.57 (m, 2H, bpy), 8.72 (m, 2H, bpy), 8.93 (m, 2H, bpy). ^{13}C NMR (75.5 MHz, acetonitrile-d_3): δ, 83.7 (C_5H_5), 84.1 (C_5H_5), 125.1, 130.2, 145.6, 147.4, 148.0 (bpy), 214.1 (CO), 217.1 (CO). IR (KBr): ν_{CO} 1925, 1957, 1986, 2002 cm^{-1}. MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix): m/z 437 ($[FpGaCl\cdot bpy]^+$, 100), 225 ($Ga\cdot bpy^+$, 43). Anal. Found: C, 36.62; H, 2.31; N, 3.56. Calc. for $C_{24}H_{18}Cl_4Fe_2Ga_2N_2O_4$: C, 36.43; H, 2.29; N, 3.54%.

*Synthesis of [FpGaCl·bpy]BPh_4 ([**3a**]BPh_4)*

To an acetonitrile (7 ml) solution of bpy (0.10 g, 0.63 mmol) and $FpGaCl_2$ (0.20 g, 0.63 mmol) was added an acetonitrile (2 ml) solution of $NaBPh_4$ (0.22 g, 0.64 mmol) at room temperature. The reaction mixture was stirred for 1 h and then filtered. The filtrate was concentrated to 2 ml and cooled to −30 °C to give orange crystals of [**3a**]BPh_4. Yield: 0.24 g (0.32 mmol, 51%). ^{1}H NMR (300 MHz, acetonitrile-d_3): δ, 5.08 (s, 5H, C_5H_5), 6.85 (t, $^{3}J_{HH} = 7.3$ Hz, 4H, BPh_4), 7.01 (dd, $^{3}J_{HH} = 7.3$ Hz, 8H, BPh_4), 7.31 (m, 8H, BPh_4), 7.99 (m, 2H, bpy), 8.42 (m, 2H, bpy), 8.50 (m, 2H, bpy), 8.88 (m, 2H, bpy). ^{13}C NMR (75.5 MHz, acetonitrile-d_3): δ, 84.1 (C_5H_5), 122.8, 126.6, 136.7, 164.8 (BPh), 125.0, 130.1, 145.6, 147.4, 148.0 (bpy), 214.2 (CO). IR (KBr): ν_{CO} 1948, 2000 cm^{-1}. MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix): m/z 437 ($[FpGaCl\cdot bpy]^+$, 100), 225 ($Ga\cdot bpy^+$, 63). Anal. Found: C, 65.30; H, 4.56; N, 3.69. Calc. for $C_{41}H_{33}BClFeGaN_2O_2$: C, 65.00; H, 4.39; N, 3.70%.

*Synthesis of [FpGaCl·phen]BPh_4 ([**3b**]BPh_4)*

Complex [**3b**]BPh_4 was synthesized as orange crystals by a procedure similar to the synthesis of [**3a**]BPh_4 using phen (0.71 g, 3.94 mmol), $FpGaCl_2$ (1.25 g, 3.94 mmol) and $NaBPh_4$ (1.35 g, 3.95 mmol). Yield: 1.45 g (1.86 mmol, 47%). ^{1}H NMR (300 MHz, acetonitrile-d_3): δ, 5.11 (s, 5H, C_5H_5), 6.84 (t, $^{3}J_{HH} = 7.3$ Hz, 4H, BPh_4), 7.02 (dd, $^{3}J_{HH} = 7.3$ Hz, 8H, BPh_4), 7.29 (m, 8H, BPh_4), 8.27 (m, 2H, phen), 8.33 (m, 2H, phen), 9.02 (m, 2H, phen), 9.28 (m, 2H, phen). ^{13}C NMR (75.5 MHz, acetonitrile-d_3): δ, 84.1 (C_5H_5), 122.7, 126.5, 136.7, 164.7 (BPh), 128.1, 128.9, 131.0, 138.8, 144.0, 149.1 (phen), 214.2 (CO). IR (KBr): ν_{CO} 1950, 1998 cm^{-1}. MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix): m/z 461 ($[FpGaCl\cdot phen]^+$, 100). Anal. Found: C, 65.65; H, 4.32; N, 3.69. Calc. for $C_{43}H_{33}BClFeGaN_2O_2$: C, 66.08; H, 4.26; N, 3.58%.

*Synthesis of [$Fp^*GaCl\cdot bpy$]$BPh_4\cdot C_7H_8$ ([**5a**]$BPh_4\cdot C_7H_8$)*

To an acetonitrile (7 ml) solution of bpy (0.041 g, 0.26 mmol) and Fp^*GaCl_2 (0.10 g, 0.26 mmol) was added an acetonitrile (2 ml) solution of $NaBPh_4$ (0.089 g, 0.26 mmol) at room temperature. The reaction mixture was stirred for 1 h and then filtered. Volatiles were removed from the filtrate under reduced pressure. The residual solid was washed with toluene (5 ml) and recrystallized from acetonitrile to afford yellow crystals of [**5a**]$BPh_4\cdot C_7H_8$. Yield: 0.12 g (0.13 mmol, 50%). ^{1}H NMR (300 MHz, acetonitrile-d_3): δ, 1.84 (s, 15H, C_5Me_5), 6.85 (t, $^{3}J_{HH} = 7.3$ Hz, 4H, BPh_4), 7.01 (dd, $^{3}J_{HH} = 7.3$ Hz, 8H,

BPh_4), 7.32 (m, 8H, BPh_4), 7.99 (m, 2H, bpy), 8.42 (m, 2H, bpy), 8.45 (m, 2H, bpy), 8.81 (m, 2H, bpy). ^{13}C NMR (75.5 MHz, acetonitrile-d_3): δ, 10.7 (C_5Me_5), 97.3 (C_5Me_5), 122.8, 126.6, 136.7, 164.8 (BPh), 125.1, 130.2, 145.5, 147.4, 147.7 (bpy), 216.2 (CO). IR (KBr): ν_{CO} 1934, 1986 cm^{-1}. MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix): m/z 507 ([Fp*GaCl·bpy]$^+$, 100), 225 (Ga·bpy$^+$, 93). Anal. Found: C, 69.01; H, 5.44; N, 3.05. Calc. for $C_{46}H_{43}BClFeGaN_2O_2 \cdot C_7H_8$: C, 69.21; H, 5.59; N, 3.05%.

*Synthesis of [Fp*GaCl·phen]BPh₄ ([**5b**]BPh₄)*

Complex [**5b**]BPh_4 was obtained as yellow crystals by a procedure similar to the synthesis of [**3a**]BPh_4 using phen (0.35 g, 1.94 mmol), Fp*$GaCl_2$ (0.50 g, 1.29 mmol) and $NaBPh_4$ (0.45 g, 1.32 mmol). THF was used as solvent instead of acetonitrile. Yield: 0.95 g (1.12 mmol, 87%). ^{1}H NMR (300 MHz, CD_3CN): δ, 1.90 (s, 15H, C_5Me_5), 6.84 (t, $^3J_{HH} = 7.3$ Hz, 4H, BPh), 7.00 (dd, $^3J_{HH} = 7.3$ Hz, 8H, BPh), 7.28 (m, 8H, BPh), 8.29 (m, 2H, phen), 8.34 (s, 2H, phen), 9.03 (m, 2H, phen), 9.23 (m, 2H, phen). ^{13}C NMR (75.5 MHz, CD_3CN): δ, 10.8 (C_5Me_5), 97.4 (C_5Me_5), 122.7, 126.6, 136.7, 164.7 (BPh), 128.2, 129.0, 131.0, 138.9, 144.0, 148.8 (phen), 216.2 (CO). IR (KBr pellet): ν_{CO} 1929, 1983 cm^{-1}. MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix): 531 ([Fp*GaCl·phen]$^+$, 100), 371 (Cp*Fe(phen)$^+$, 30). Anal. Found: C, 67.72; H, 5.35; N, 3.28. Calc. for $C_{48}H_{43}BClFeGaN_2O_2$: C, 67.69; H, 5.09; N, 3.29%.

*Synthesis of [Fp*GaS^{p}Tol·phen]BPh₄ ([**6**]BPh₄)*

Method 1: a suspension of NaS^{p}Tol prepared from HS^{p}Tol (30 mg, 0.24 mmol) and NaH (6 mg, 0.25 mmol) in THF (3 ml) was added slowly to a THF (15 ml) solution of [Fp*GaCl·phen]BPh_4 ([**5b**]BPh_4, 185 mg, 0.217 mmol) at −96 °C with vigorous stirring. The reaction mixture was stirred for 30 min at −98 °C, then allowed to warm to room temperature, and filtered. The filtrate was concentrated to 3 ml and cooled to −50 °C to give yellow crystals of [**6**]BPh_4. Yield: 71 mg (76 μmol, 35%).

Method 2: a THF (5 ml) solution of Me_3SiS^pTol (300 μl, 0.29 g, 1.46 mmol) was added to a THF (20 ml) solution of [**5b**]BPh_4 (0.40 g, 0.47 mmol) at room temperature and stirred for 40 min. Volatiles were removed from the reaction mixture under reduced pressure. Yellow crystals of [**6**]BPh_4 were washed with hexane and dried under reduced pressure. Yield: 0.44 g (0.47 mmol, 99%). ^{1}H NMR (300 MHz, CD_3CN): δ, 1.77 (s, 3H, *p*-Me), 1.99 (s, 15H, C_5Me_5), 5.91 (m, 2H, ^{p}Tol), 5.96 (m, 2H, ^{p}Tol), 6.85 (t, $^3J_{HH} = 7.3$ Hz, 4H, BPh), 7.00 (dd, $^3J_{HH} = 7.3$ Hz, 8H, BPh), 7.28 (m, 8H, BPh), 8.06 (s, 2H, phen), 8.21 (m, 2H, phen), 8.83 (m, 2H, phen), 9.17 (m, 2H,

Table 1. Crystal data and structure refinement for [Fp*GaCl·phen]$BPh_4 \cdot 2CH_3CN$ and [FpGaS^{p}Tol·phen]BPh_4 ([**5b**]$BPh_4 \cdot 2CH_3CN$ and [**6**]BPh_4 respectively)

	[**5b**]$BPh_4 \cdot 2CH_3CN$	[**6**]BPh_4
Empirical formula	$C_{52}H_{49}BClFeGaN_4O_2$	$C_{55}H_{50}BFeGaN_2O_2S$
Formula weight	933.78	939.41
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/a$
Unit cell dimensions		
a (Å)	13.8222(6)	18.0610(7)
b (Å)	21.7485(10)	15.4102(7)
c (Å)	15.2061(7)	18.1733(7)
β (°)	91.4712(8)	111.6261(18)
Volume (Å^3)	4569.6(4)	4702.0(3)
Z	4	4
Density (calculated) (g cm^{-3})	1.357	1.327
Absorption coefficient (mm^{-1})	1.011 mm^{-1}	0.970
$F(000)$	1936	1952
Crystal size (mm^3)	0.35 × 0.15 × 0.05	0.3 × 0.3 × 0.1
Reflections collected	38 120	39 848
Independent reflections	10 115 ($R_{int} = 0.0578$)	10 601 ($R_{int} = 0.0767$)
Reflections with $I > 2\sigma(I)$	8339	8824
Data/restraints/parameters	10 115/0/559	10 601/0/574
Goodness-of-fit on F^2	1.120	1.140
Final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0418$, $wR_2 = 0.1036$	$R_1 = 0.0496$, $wR_2 = 0.1206$
R indices (all data)[a]	$R_1 = 0.0574$, $wR_2 = 0.1114$	$R_1 = 0.0661$, $wR_2 = 0.1363$
Largest diff. peak and hole (e$^-$ Å^{-3})	0.478 and −0.592	0.461 and −0.652

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{0.5}$.

phen). ^{13}C NMR (75.5 MHz, CD_3CN): δ, 11.1 (C_5Me_5), 20.2 (*p*-Me), 97.3 (C_5Me_5), 122.7, 126.6, 136.7, 164.7 (BPh), 127.8, 133.5 (^{p}Tol), 128.1, 128.8, 133.5, 139.3, 142.9, 148.3 (phen), 217.0 (CO). IR (KBr pellet): ν_{CO} 1923, 1977 cm^{-1}. MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix): 619 ([Fp*GaS^{p}Tol·phen]$^+$, 100), 371 (Cp*Fe(phen)$^+$, 32). Anal. Found: C, 70.33; H, 5.52; N, 2.93. Calc. for $C_{55}H_{50}BClFeGaN_2O_2S$: C, 70.32; H, 5.36; N, 2.98%.

Structure determination

Single crystals of [**5b**]$BPh_4 \cdot 2CH_3CN$ and [**6**]BPh_4 suitable for X-ray crystal structure analysis were obtained by recrystallization of [**5b**]BPh_4 from CH_3CN and of [**6**]BPh_4 from THF respectively. The intensity data were collected on a RIGAKU RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation to a maximum 2θ value of 55.0° at 150 K. A total of 44 images, corresponding to 220.0° oscillation angles, were collected with two different goniometer settings. Exposure times were 1.3 min and 0.7 min per degree for [**5b**]$BPh_4 \cdot 2CH_3CN$ and [**6**]BPh_4 respectively. Readout was performed in the 0.100 mm pixel mode. Absorption correction was applied numerically based on the crystal shape for [**5b**]$BPh_4 \cdot 2CH_3CN$, and empirically for [**6**]BPh_4. Crystallographic data are listed in Table 1. The structures were solved by Patterson and Fourier transform methods. All non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic displacement parameters based on F^2 with all reflections. All hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. The final residue R_1 and the weighted wR_2 were $R_1 = 0.0418$ and $wR_2 = 0.1036$ for 8339 refractions with $I > 2\sigma(I)$ for [**5b**]$BPh_4 \cdot 2CH_3CN$, and $R_1 = 0.0496$ and $wR_2 = 0.1206$ for 8824 refractions with $I > 2\sigma(I)$ for [**6**]BPh_4. All calculations were performed using SHELX[32,33] on an Apple Macintosh computer.

The crystallographic data for the structure of [**5b**]$BPh_4 \cdot 2CH_3CN$ and [**6**]BPh_4 have been deposited with the Cambridge Crystallographic Data Centre as CCDC nos 197528 and 197529 respectively. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk; or www: http://www.ccdc.cam.ac.uk).

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